

# PATENT ABSTRACTS OF JAPAN

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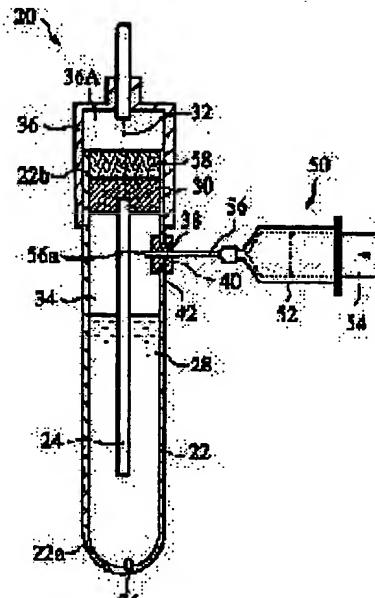
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## (54) PRESSURIZATION-TYPE REFERENCE ELECTRODE

### (57)Abstract:

**PURPOSE:** To provide a pressurization-type reference electrode with low manufacturing cost, excellent productivity, and high performance which can be used singly or so as to be built in a combined electrode by a method wherein the inside pressure of the reference electrode can be adjusted arbitrarily as desired and, even when a pressure is decreased while the reference electrode is used for a measurement, the reference electrode can be pressurized repeatedly.

**CONSTITUTION:** A pressurization-type reference electrode 20 comprises a side-face packing 40 installed in such a way that it is situated on the side face of an outer tube 22 and in an upper-part air chamber 34 at an inside liquid 28 housed in the outer tube. A needle-shaped pipe 56 is pierced through the side-face packing 40 so as to be freely pierced and pulled out, and compressed air is injected into the upper-part air chamber 34 in the outer tube so as to be capable of being pressurized.



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CLAIMS

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## [Claim(s)]

[Claim 1] The outer case which closed the lower part edge, carried out opening of the upper part edge, and held internal liquid in the interior, The internal electrode with which it has been arranged the liquid junction prepared in the lower part edge of an outer case, and inside an outer case, the upper part edge was held by up packing inserted in the interior of an outer case by suiting, and the lower part part was immersed in internal liquid, Are the reference electrode which \*\*\*\*, and on the side face of said outer case, as it is located in the upper part air chamber of the internal liquid held in said outer case, side -face packing is installed. The pressure type reference electrode characterized by having extracted the needlelike pipe to this side-face packing, having stabbed it with it, having thrust free, having injected the compressed air into the upper part air chamber of said outer case, and enabling pressurization of this air chamber.

[Claim 2] Said pressure type reference electrode is a pressure type reference electrode of claim 1 characterized by being annularly arranged in the said alignment around the measuring electrode equipped with the induction film.

[Claim 3] Claim 1 or 2 pressure type reference electrodes which are filled up with adhesives on said up packing, and fix up packing to the location.

[Claim 4] Said side-face packing is claims 1 and 2 or the pressure type reference electrode of 3 produced with the electrical insulation material which has rubber elasticity.

[Claim 5] Said electrical insulation material is the pressure type reference electrode of claim 4 which is nitrile rubber (NBR), chloroprene rubber (CR), ethylene propylene rubber (EPM), silicone rubber (Si), a fluororubber (FPM), or isobutylene isoprene rubber.

[Claim 6] Said liquid junction is a pressure type reference electrode given in one term of claims 1-5 which are the porosity polyethylene which has absorptivity, porosity polyester, or a porosity acrylic.

[Claim 7] Said liquid junction is a pressure type reference electrode given in one term of claims 1-5 whose water absorption is the porous ceramics made into 5 - 15%.

[Claim 8] Said internal liquid is a pressure type reference electrode given in one term of claims 1-7 which are a water solution or gel liquid.

[Claim 9] Said gel liquid is the pressure type reference electrode of claim 8 which is the potassium chloride solution gelled by hydroxyethyl cellulose, the carboxymethyl cellulose, or the acrylamide polymer.

[Claim 10] The outer case which closed the lower part edge, carried out opening of the upper part edge, and held internal liquid in the interior, The internal electrode with which it has been arranged the liquid junction prepared in the lower part edge of an outer case, and inside an outer case, the upper part edge was held by up packing inserted in the interior of an outer case by suiting, and the lower part part was immersed in internal liquid, The pressure type reference electrode which is a reference electrode which \*\*\*\* and is characterized by having extracted the needlelike pipe to said up packing, having stabbed it with it, having thrust free, having injected the compressed air into the upper part air chamber of said outer case, and enabling pressurization of this air chamber.

[Claim 11] Said pressure type reference electrode is a pressure type reference electrode of claim 10 characterized by being annularly arranged in the said alignment around the measuring electrode equipped with the induction film.

[Claim 12] Claim 10 or 11 pressure type reference electrodes which are filled up with adhesives on said up packing, and fix up packing to the location.

[Claim 13] Said up packing is claims 10 and 11 or the pressure type reference electrode of 12 produced with the electrical insulation material which has rubber elasticity.

[Claim 14] Said electrical insulation material is the pressure type reference electrode of claim 13 which is nitrile rubber (NBR), chloroprene rubber (CR), ethylene propylene rubber (EPM), silicone rubber (Si), a fluororubber (FPM), or isobutylene isoprene rubber.

[Claim 15] Said liquid junction is a pressure type reference electrode given in one term of claims 10-14 which are the porosity polyethylene which has absorptivity, porosity polyester, or a porosity acrylic.

[Claim 16] Said liquid junction is a pressure type reference electrode given in one term of claims 10-14 whose water absorption is the porous ceramics made into 5 - 15%.

[Claim 17] Said internal liquid is a pressure type reference electrode given in one term of claims 10-16 which are a water solution or gel liquid.

[Claim 18] Said gel liquid is the pressure type reference electrode of claim 17 which is the potassium chloride solution gelled by hydroxyethyl cellulose, the carboxymethyl cellulose, or the acrylamide polymer.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the reference electrode of a pressure type with which the internal liquid of a reference electrode was especially pressurized about the reference electrode used for measurement of pH, ion concentration, etc. by fermentation industry, the chemical industry, etc. The reference electrode of this invention is used by the pair with the measuring electrode equipped with pH or an ion sensing membrane, or is used as a composite electrode with which the reference electrode was built into a measuring electrode and one.

[0002]

[Description of the Prior Art] Conventionally, measurement of pH, ion concentration, etc. is frequently performed in various fields, with the measuring electrode equipped with pH or an ion sensing membrane, a pair is made for this measurement and a reference electrode is used for it. Moreover, the composite electrode with which the reference electrode was built into a measuring electrode and one may be used.

[0003] Especially, in fermentation industry and the chemical industry, if process liquid flows backwards inside a reference electrode from the liquid junction of a reference electrode when measuring process liquid with a pressure, the concentration of internal liquid will change and the blinding of liquid junction will happen further. The following various attempts are made in order to solve such a problem.

[0004] That is, the 1st approach is set to the composite electrode equipped with the measuring electrode 2 equipped with induction film 2a, and the reference electrode 6 annularly arranged in the said alignment to this measuring electrode 2, as shown in drawing 5. It is the approach of pressurizing the interior liquid of a reference electrode at a predetermined pressure by connecting the compressed -air source of supply which consists of a pump 201 and a valve 202 to the tank 200 with which internal liquid is supplied to the reference electrode 6 of every exception, supplying the compressed air, and making the inside of a tank 200 into a predetermined pressure. By pressurizing the interior liquid of a reference electrode, it is prevented that process liquid flows backwards into a reference electrode 6 through liquid junction 26.

[0005] The 2nd approach is shown in drawing 6. According to this approach, the electrode cage 203 holding a composite electrode is made into an airtight structure, and this electrode cage 203 and the up space section of a reference electrode 6 are opened for free passage. The electrode cage 203 is connected with the compressed-air source of supply which consists of a valve 202 and a pump 201 through a check valve 204, and the internal liquid upper part is maintained by place constant pressure. It is prevented that process liquid flows backwards into a reference electrode through liquid junction 26 by this.

[0006] The 3rd approach is an approach which is indicated by JP,6-35950,B and indicated by drawing 7 of this application attachment. That is, according to this approach, the upper part of the reference electrode 6 annularly formed in the surroundings of a measuring electrode 2 is sealed, and a gas supply line 205 is attached in that part. This gas supply line 205 is connected with the compressed-air source of supply which consists of a valve 202 and a pump 201 at the time of electrode manufacture, and the

compressed air of place constant pressure is supplied to the reference electrode annular interior of a room. Then, a gas supply line 205 is blocked airtightly and a compressed-air source of supply is removed. The reference electrode annular interior of a room, i.e., the internal liquid upper part, is maintained by place constant pressure, and a back flow into the reference electrode of the process liquid through the liquid junction 26 for use is prevented by this.

[0007]

[Problem(s) to be Solved by the Invention] However, the 1st and 2nd approaches of the above are 0.5 kg/cm<sup>2</sup> [ the comparatively high pressure ]. Although used in the above (gage pressure) process, in order to hold the compressed air, the airtight internal liquid tank 200 and the electrode cage 203 are required. Moreover, on the occasion of use, it needs a compressed-air source of supply etc., and an electrode price not only becomes high, but piping between an electrode and a compressed-air source of supply is still more indispensable, and there is a problem in the operability of an electrode, and handling nature.

[0008] Moreover, as for the 3rd approach of the above, a compressed -air source of supply and compressed-air charging line equipment are needed at the time of manufacture of an electrode. Furthermore, the gas supply line 205 prepared in a reference electrode 6 is used as a platinum capillary tube, and needs the skilled special operator to whom it is not only expensive, but this gas supply line 205 is made as for glass blowing to attaching in a glass reference electrode formation wall. Thus, not only a manufacturing cost is high, but the electrode according to this approach has a problem in respect of productivity.

[0009] The purpose of this invention does not have the need for a compressed -air source of supply, compressed-air charging line equipment, etc. at the time of manufacture of an electrode, and a special skillful operator does not need, either, but a manufacturing cost is cheap, it is [ productivity is also good, ] highly efficient, and using it independently is also offering the pressure type reference electrode which can also be used being able to include in a composite electrode.

[0010] The manufacturing cost which can be repeatedly pressurized also when there is pressure reduction, while other purposes of this invention can adjust the internal pressure of a reference electrode to arbitration according to a request and it is used for measurement is cheap, and productivity is also good and it is offering the pressure type reference electrode which the highly efficient thing used independently can also use for a composite electrode, incorporating.

[0011]

[Means for Solving the Problem] The above-mentioned purpose is attained by the pressure type reference electrode concerning this invention. The outer case which this invention closed the lower part edge, carried out opening of the upper part edge, and held internal liquid in the interior when summarizing, The internal electrode with which it has been arranged the liquid junction prepared in the lower part edge of an outer case, and inside an outer case, the upper part edge was held by up packing inserted in the interior of an outer case by suiting, and the lower part part was immersed in internal liquid, Are the reference electrode which \*\*\*\*, and on the side face of said outer case, as it is located in the upper part air chamber of the internal liquid held in said outer case, side-face packing is installed. It is the pressure type reference electrode characterized by having extracted the needlelike pipe to this side-face packing, having stabbed it with it, having thrust free, having injected the compressed air into the upper part air chamber of said outer case, and enabling pressurization of this air chamber.

[0012] The outer case which according to other modes of this invention closed the lower part edge, carried out opening of the upper part edge, and held internal liquid in the interior, The internal electrode with which it has been arranged the liquid junction prepared in the lower part edge of an outer case, and inside an outer case, the upper part edge was held by up packing inserted in the interior of an outer case by suiting, and the lower part part was immersed in internal liquid, It is the reference electrode which \*\*\*\* and the pressure type reference electrode characterized by having extracted the needlelike pipe to said up packing, having stabbed it with it, having thrust free, having injected the compressed air into the upper part air chamber of said outer case, and enabling pressurization of this air chamber is offered.

[0013] Annular arrangement of the above -mentioned pressure type reference electrode of this invention can also be carried out in the said alignment around the measuring electrode equipped with the induction

film. Preferably, it is filled up with adhesives on said up packing, and up packing is fixed to the location.

[0014] Packing which extracts and stabs a needlelike pipe and pierces it free in this invention is produced with the electrical insulation material which has rubber elasticity, for example, let it be nitrile rubber (NBR), chloroprene rubber (CR), ethylene propylene rubber (EPM), silicone rubber (Si), a fluororubber (FPM), or isobutylene isoprene rubber. Moreover, said liquid junction has the desirable porous ceramics with which it can also consider as the porosity polyethylene which has absorptivity, porosity polyester, or a porosity acrylic, and water absorption is especially made into 5 - 15%.

[0015] Furthermore, said internal liquid to be used is used as a water solution or gel liquid, and let said gel liquid be the potassium chloride solution gelled by hydroxyethyl cellulose, the carboxymethyl cellulose, or the acrylamide polymer.

[0016]

[Example] Hereafter, the pressure type reference electrode concerning this invention is \*\*(ed) in the example, and is explained in more detail.

[0017] Reference of example 1 drawing 1 shows one example of the pressure type reference electrode 20 concerning this invention. In this example, the pressure type reference electrode 20 is used as a glass electrode, lower part edge 22a closes it, upper part edge 22b is equipped with the glass tube (outer case) 22 which carried out opening, and liquid junction 26 is installed in lower part edge 22a. Moreover, as an internal electrode 24 is arranged inside an outer case 22 and the lower part part of this internal electrode 24 is immersed, internal liquid (reference electrolytic solution) 28 is held.

[0018] The lead wire 32 which the upper part edge of an internal electrode 24 is held at the up packing 30 inserted in the interior of an outer case 22 by suiting, and was connected to the internal electrode 24 penetrates this up packing 30, and is taken out outside. As for an internal electrode 24, at this time, it is desirable not to penetrate the up packing 30, but to insert even in abbreviation one half extent of the thickness of the up packing 30, and to make it only lead wire 32 penetrate the up packing 30. This is for preventing that an internal electrode 24 is put back up, when it is filled up with the compressed air in an outer case 22 and the upper part air chamber 34 of internal liquid 28 is pressurized so that it may be for protecting and may mention later that an internal electrode 24 runs through the up packing 30, and projects upwards when stuffing the up packing 30 into the interior of an outer case 22. Upper part open end 22b of an outer case 22 is closed by cap 36.

[0019] In this example, a stoma 38 is drilled in the side face of an outer case 22, and the side -face packing 40 is attached in this hole 38. It is made for the attaching position of the side -face packing 40 to be located in the upper part air chamber 34 of the internal liquid 28 held in the outer case 22. Moreover, although side-face packing 40 can be made into the configuration of arbitration, in this example, it considers as the shape of a cylindrical shape in which the circular sulcus 42 for attaching in the stoma 38 of an outer case 22 was formed, and is produced with a spring material. Therefore, the outer diameter of a circular sulcus 42 is made larger than the bore of the outer case stoma 38, therefore the side -face packing 40 fits into this stoma 38 in a from cartridge, and is fixed to it.

[0020] In the reference electrode 20 of this invention of the above -mentioned configuration, the upper part air chamber 34 of an outer case 22 is pressurized using a compressed -air supply means 50 like a syringe (syringe). That is, according to this example, the compressed -air supply means 50 has a cylinder 52 and the piston 54 which fitted into this cylinder 52 free [ sliding ], and the needlelike pipe 56 which cut a tip like a hypodermic needle aslant is attached at the tip of a cylinder 52. Therefore, this needlelike pipe 56 can reach to the upper part air chamber 34 of an outer case 22 by thrusting that tip section 56a into the side-face packing 40 which is an elastic body, as shown in drawing 1 . By operating a piston 54 in the direction of an arrow head after that, the compressed air is injected into the upper part air chamber 34 through this needlelike pipe 56, and this air chamber 34 is pressurized.

[0021] After an air chamber 34 serves as a predetermined pressure, the needlelike pipe 56 is sampled from the side-face packing 40. Since the side-face packing 40 is an elastic body at this time, the hole after extracting the needlelike pipe 56 will be closed with that elasticity. That is, the side -face packing 40 plays the role of a check valve.

[0022] Although the side-face packing 40 which makes the function like \*\*\*\* can be produced using the thing of arbitration if it is an electrical insulation material which has rubber elasticity by 2 -30mm in thickness, it has nitrile rubber (NBR), chloroprene rubber (CR), ethylene propylene rubber (EPM), silicone rubber (Si), a fluororubber (FPM), etc., for example. In addition, since it has exposed into atmospheric air, as for the external surface of the side-face packing 40, it is desirable at this example to produce by the small elastomer of gas permeability (polymeric materials which have rubber-like elasticity), for example, isobutylene isoprene rubber.

[0023] moreover, although various dimension configurations of the side-face packing 40 could be boiled and designed, the good result was able to be obtained by considering as the outer diameter of 5-10mm, and die length of 3-10mm.

[0024] On the other hand, when the high ingredient of gas permeability is used like silicone rubber as an ingredient of said up packing 30, as shown in drawing 1, it is desirable to be filled up with adhesives 58 on the up packing 30, and it is desirable as adhesives for restoration also in this case, few ingredients, for example, the epoxy resin adhesive, of gas permeability. According to this invention persons' experimental result, silicone system adhesives had large gas permeability, for example, it turned out that the air of 3 kg/cm<sup>2</sup> (gage pressure) will fall even to 1 kg/cm<sup>2</sup> (gage pressure) in three days. On the other hand, even if epoxy resin adhesive passed on the 3rd, there was no fall of a pressure substantially. Furthermore, building envelope 36A formed with cap 36 if needed can also be filled up with the same thing as the above-mentioned adhesives for restoration.

[0025] Although a water solution or gel liquid is sufficient as the internal liquid 28 held in an outer case 22 with the reference electrode 20 of this invention, the gel liquid of the pressure percentage reduction of the outer case air chamber 34 is smaller. As gel liquid, there is a potassium chloride solution gelled, for example by hydroxyethyl cellulose, the carboxymethyl cellulose, or the acrylamide polymer.

[0026] Moreover, liquid junction 26 has the high resistance to a pressure, and if it is the good ingredient of absorptivity, it is producible using the thing of arbitration. For example, the porosity polyethylene which has absorptivity, porosity polyester, a porosity acrylic, etc. can be used. Especially the porous ceramics with which water absorption is made into 5 - 15% are especially effective from being repeatedly exposed to a 120-130-degree C elevated-temperature steam for sterilization, when using the reference electrode 20 of this invention in fermentation industry etc. in addition, the volume (V<sub>0</sub>) of \*\*\*\* [ as opposed to / with water absorption / the volume (V) of the whole liquid junction 26 with this application specification ] -- comparatively (V<sub>0</sub> / V) -- meaning .

[0027] In this example, the ceramics of 10% of water absorption was able to be used for liquid junction 26, the potassium chloride solution gelled as internal liquid 28 at hydroxyethyl cellulose was able to be used, and the result with the good time of producing the side-face packing 40 by penetrable small isobutylene isoprene rubber was still more specifically able to be obtained. Moreover, when the internal pressure after fixed time amount progress declined, again, the needlelike pipe 56 was able to be thrust into the side-face packing 40, and it was able to pressurize.

[0028] As mentioned above, since extract the needlelike pipe 56 to the packing 40 which was fixed according to this example, stab it with it, it thrusts free, the compressed air is poured in and the needlelike pipe 56 is considered as the configuration extracted after that, pressures are 2.5 kg/cm<sup>2</sup>. If it is less than, the disposable syringe of a low price can be used without using a large-sized compressed-air feeder like a compressor. Especially in this example which attached packing 40 in the lateral portion of the reference electrode outer case 22, while using this reference electrode 20 for measurement, also when there is pressure reduction, it can pressurize repeatedly.

[0029] One example when the pressure type reference electrode 20 concerning this invention is used for example 2 drawing 2 by the composite electrode 1 is shown.

[0030] The pressure type composite electrode 1 is used as a glass electrode in this example, and it has the container liner 4 which constitutes the measuring electrode 2 equipped with induction film 2a, and the outer case 22 which constitutes the reference electrode 20 arranged in the said alignment to this container liner 4.

[0031] The buffer solution 8 is held in the internal room 6 formed with a container liner 4 in order to

form a measuring electrode 2, and an electrode 10 is arranged in it. The lead wire 14 which penetrates the plug 12 which closes the upper part of the internal room 6, and extends is connected to this electrode 10. Moreover, internal liquid (reference electrolytic solution) 28 is held in the annular room 34 formed with a container liner 4 and an outer case 22 in order to form a reference electrode 20, and an internal electrode 24 is arranged. Liquid junction 26 is formed in the lower part edge of the annular room 34.

[0032] The internal electrode 24 is attached in the annular up packing 30 inserted in the annular room 34 by suiting in this example. Moreover, the lead wire 32 connected to the internal electrode 24 penetrates this up packing 30, and is taken out outside. At this time, it is desirable for an internal electrode 24 not to penetrate the up packing 30, but to insert it to the abbreviation one half of the thickness of the up packing 30 for the reason explained in the example 1, and to make it only lead wire 32 penetrate the up packing 30.

[0033] Also in this example, as it is similarly located in the side face of an outer case 22 with the example 1 having explained at the especially annular air chamber 34, the side-face packing 40 is formed. An ingredient, a dimension configuration, the compressed-air supply means 50, etc. of the side -face packing 40 are made the same as an example 1, and the explanation beyond this is omitted.

[0034] Also in this example, the same operation effectiveness as an example 1 can be acquired.

[0035] Other examples of the pressure type reference electrode 20 built over this invention at example 3 drawing 3 are shown.

[0036] Although the pressure type reference electrode 20 of this example is considered as the same configuration as the reference electrode 1 of the example 1 shown in drawing 1 , every time the side-face packing 40 of an example 1 is formed, it does not break it, but merely differ in that installation of the compressed air into the air chamber 34 of a reference electrode 20 is performed through the up packing 30. Therefore, in this example, the up packing 30 is produced with the above -mentioned spring material like the same elastomer as the side-face packing 40 of an example 1 which has rubber elasticity.

[0037] Moreover, in this example, since the needlelike pipe 56 of the compressed-air supply means 50 is considered as the configuration thrust into the up packing 30, before installing cap 36 in the reference electrode upper part, pressurization in the annular room 34 is performed.

[0038] Furthermore, when having already filled up with the adhesives 58 for up packing immobilization, in order for the needlelike pipe 56 to also make these adhesives 58 penetrate, even if adhesives 58 are after hardening, it is required that it should have rubber elasticity. Therefore, as adhesives 58, silicone resin is suitable.

[0039] Also in this example, the same operation effectiveness as an example 1 can be acquired.

[0040] Other examples when the pressure type reference electrode 20 concerning this invention is used for example 4 drawing 4 by the composite electrode are shown.

[0041] The pressure type composite electrode 1 of this example is considered as the same configuration as the composite electrode 1 of the example 2 shown in drawing 2 , and every time the side -face packing 40 of an example 2 is formed, it does not break it, but they merely differ in that installation of the compressed air into the annular room 34 of a reference electrode 20 is performed through the up packing 30. Therefore, the up packing 30 is produced with the above -mentioned spring material like an elastomer like [ this example ] the case of an example 3.

[0042] Moreover, in this example, since the needlelike pipe 56 of the compressed-air supply means 50 is considered as the configuration thrust into the up packing 30 like the case of an example 3, before installing cap 36 in the composite electrode upper part, pressurization in the annular room 34 is performed.

[0043] Furthermore, also in this example, when having already filled up with the adhesives 58 for up packing immobilization, in order for the needlelike pipe 56 to also make these adhesives 58 penetrate, even if adhesives 58 are after hardening, it is required that it should have rubber elasticity. Therefore, as adhesives 58, silicone resin is suitable.

[0044] Also in this example, the same operation effectiveness as an example 2 can be acquired.

[0045]

[Effect of the Invention] As explained above, the pressure type reference electrode of this invention Since a needlelike pipe is thrust into fixed packing, the compressed air is poured in and a needlelike pipe is considered as the configuration extracted after that When the annular indoor pressure of a reference electrode can be adjusted to arbitration according to a request and packing is especially attached in the lateral portion of a reference electrode outer case While using this reference electrode for measurement, also when there is pressure reduction, it can pressurize repeatedly and has the features of being highly efficient. And for the pressure type reference electrode of this invention, a special skillful operator cannot need, either, and can manufacture, a manufacturing cost is cheap, and productivity is also good, and pressures are 2.5 kg/cm<sup>2</sup>. If it is less than, the disposable syringe of a low price can be used without using a large-sized compressed-air feeder like a compressor, and it is very useful.

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**TECHNICAL FIELD**

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**[Industrial Application]** This invention relates to the reference electrode of a pressure type with which the internal liquid of a reference electrode was especially pressurized about the reference electrode used for measurement of pH, ion concentration, etc. by fermentation industry, the chemical industry, etc. The reference electrode of this invention is used by the pair with the measuring electrode equipped with pH or an ion sensing membrane, or is used as a composite electrode with which the reference electrode was built into a measuring electrode and one.

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## PRIOR ART

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[Description of the Prior Art] Conventionally, measurement of pH, ion concentration, etc. is frequently performed in various fields, with the measuring electrode equipped with pH or an ion sensing membrane, a pair is made for this measurement and a reference electrode is used for it. Moreover, the composite electrode with which the reference electrode was built into a measuring electrode and one may be used.

[0003] Especially, in fermentation industry and the chemical industry, if process liquid flows backwards inside a reference electrode from the liquid junction of a reference electrode when measuring process liquid with a pressure, the concentration of internal liquid will change and the blinding of liquid junction will happen further. The following various attempts are made in order to solve such a problem.

[0004] That is, the 1st approach is set to the composite electrode equipped with the measuring electrode 2 equipped with induction film 2a, and the reference electrode 6 annularly arranged in the said alignment to this measuring electrode 2, as shown in drawing 5. It is the approach of pressurizing the interior liquid of a reference electrode at a predetermined pressure by connecting the compressed -air source of supply which consists of a pump 201 and a valve 202 to the tank 200 with which internal liquid is supplied to the reference electrode 6 of every exception, supplying the compressed air, and making the inside of a tank 200 into a predetermined pressure. By pressurizing the interior liquid of a reference electrode, it is prevented that process liquid flows backwards into a reference electrode 6 through liquid junction 26.

[0005] The 2nd approach is shown in drawing 6. According to this approach, the electrode cage 203 holding a composite electrode is made into an airtight structure, and this electrode cage 203 and the up space section of a reference electrode 6 are opened for free passage. The electrode cage 203 is connected with the compressed-air source of supply which consists of a valve 202 and a pump 201 through a check valve 204, and the internal liquid upper part is maintained by place constant pressure. It is prevented that process liquid flows backwards into a reference electrode through liquid junction 26 by this.

[0006] The 3rd approach is an approach which is indicated by JP,6-35950,B and indicated by drawing 7 of this application attachment. That is, according to this approach, the upper part of the reference electrode 6 annularly formed in the surroundings of a measuring electrode 2 is sealed, and a gas supply line 205 is attached in that part. This gas supply line 205 is connected with the compressed-air source of supply which consists of a valve 202 and a pump 201 at the time of electrode manufacture, and the compressed air of place constant pressure is supplied to the reference electrode annular interior of a room. Then, a gas supply line 205 is blocked airtightly and a compressed-air source of supply is removed. The reference electrode annular interior of a room, i.e., the internal liquid upper part, is maintained by place constant pressure, and a back flow into the reference electrode of the process liquid through the liquid junction 26 for use is prevented by this.

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**EFFECT OF THE INVENTION**

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**[Effect of the Invention]** As explained above, it is the pressure type reference electrode of this invention, Since it considered as the configuration which thrusts a needlelike pipe into fixed packing, pours in the compressed air, and extracts a needlelike pipe after that, when the annular indoor pressure of a reference electrode can be adjusted to arbitration according to a request and packing is especially attached in the lateral portion of a reference electrode outer case, while using this reference electrode for measurement, also when there is pressure reduction, it can pressurize repeatedly and has the features of being highly efficient. And for the pressure type reference electrode of this invention, a special skillful operator cannot need, either, and can manufacture, a manufacturing cost is cheap, and productivity is also good, and pressures are 2.5 kg/cm<sup>2</sup>. If it is less than, the disposable syringe of a low price can be used without using a large-sized compressed-air feeder like a compressor, and it is very useful.

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### TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, the 1st and 2nd approaches of the above are 0.5 kg/cm<sup>2</sup> [ the comparatively high pressure ]. Although used in the above (gage pressure) process, in order to hold the compressed air, the airtight internal liquid tank 200 and the electrode cage 203 are required. Moreover, on the occasion of use, it needs a compressed-air source of supply etc., and an electrode price not only becomes high, but piping between an electrode and a compressed-air source of supply is still more indispensable, and there is a problem in the operability of an electrode, and handling nature.

[0008] Moreover, as for the 3rd approach of the above, a compressed-air source of supply and compressed-air charging line equipment are needed at the time of manufacture of an electrode. Furthermore, the gas supply line 205 prepared in a reference electrode 6 is used as a platinum capillary tube, and needs the skilled special operator to whom it is not only expensive, but this gas supply line 205 is made as for glass blowing to attaching in a glass reference electrode formation wall. Thus, not only a manufacturing cost is high, but the electrode according to this approach has a problem in respect of productivity.

[0009] The purpose of this invention does not have the need for a compressed-air source of supply, compressed-air charging line equipment, etc. at the time of manufacture of an electrode, and a special skillful operator does not need, either, but a manufacturing cost is cheap, it is [ productivity is also good, ] highly efficient, and using it independently is also offering the pressure type reference electrode which can also be used being able to include in a composite electrode.

[0010] The manufacturing cost which can be repeatedly pressurized also when there is pressure reduction, while other purposes of this invention can adjust the internal pressure of a reference electrode to arbitration according to a request and it is used for measurement is cheap, and productivity is also good and it is offering the pressure type reference electrode which the highly efficient thing used independently can also use for a composite electrode, incorporating.

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[Translation done.]

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## MEANS

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[Means for Solving the Problem] The above-mentioned purpose is attained by the pressure type reference electrode concerning this invention. The outer case which this invention closed the lower part edge, carried out opening of the upper part edge, and held internal liquid in the interior when summarizing, The internal electrode with which it has been arranged the liquid junction prepared in the lower part edge of an outer case, and inside an outer case, the upper part edge was held by up packing inserted in the interior of an outer case by suiting, and the lower part part was immersed in internal liquid, Are the reference electrode which \*\*\*\*, and on the side face of said outer case, as it is located in the upper part air chamber of the internal liquid held in said outer case, side-face packing is installed. It is the pressure type reference electrode characterized by having extracted the needlelike pipe to this side-face packing, having stabbed it with it, having thrust free, having injected the compressed air into the upper part air chamber of said outer case, and enabling pressurization of this air chamber.

[0012] The outer case which according to other modes of this invention closed the lower part edge, carried out opening of the upper part edge, and held internal liquid in the interior, The internal electrode with which it has been arranged the liquid junction prepared in the lower part edge of an outer case, and inside an outer case, the upper part edge was held by up packing inserted in the interior of an outer case by suiting, and the lower part part was immersed in internal liquid, It is the reference electrode which \*\*\*\* and the pressure type reference electrode characterized by having extracted the needlelike pipe to said up packing, having stabbed it with it, having thrust free, having injected the compressed air into the upper part air chamber of said outer case, and enabling pressurization of this air chamber is offered.

[0013] Annular arrangement of the above-mentioned pressure type reference electrode of this invention can also be carried out in the said alignment around the measuring electrode equipped with the induction film. Preferably, it is filled up with adhesives on said up packing, and up packing is fixed to the location.

[0014] Packing which extracts and stabs a needlelike pipe and pierces it free in this invention is produced with the electrical insulation material which has rubber elasticity, for example, let it be nitrile rubber (NBR), chloroprene rubber (CR), ethylene propylene rubber (EPM), silicone rubber (Si), a fluororubber (FPM), or isobutylene isoprene rubber. Moreover, said liquid junction has the desirable porous ceramics with which it can also consider as the porosity polyethylene which has absorptivity, porosity polyester, or a porosity acrylic, and water absorption is especially made into 5 - 15%.

[0015] Furthermore, said internal liquid to be used is used as a water solution or gel liquid, and let said gel liquid be the potassium chloride solution gelled by hydroxyethyl cellulose, the carboxymethyl cellulose, or the acrylamide polymer.

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### EXAMPLE

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[Example] Hereafter, the pressure type reference electrode concerning this invention is \*\*(ed) in the example, and is explained in more detail.

[0017] Reference of example 1 drawing 1 shows one example of the pressure type reference electrode 20 concerning this invention. In this example, the pressure type reference electrode 20 is used as a glass electrode, lower part edge 22a closes it, upper part edge 22b is equipped with the glass tube (outer case) 22 which carried out opening, and liquid junction 26 is installed in lower part edge 22a. Moreover, as an internal electrode 24 is arranged inside an outer case 22 and the lower part part of this internal electrode 24 is immersed, internal liquid (reference electrolytic solution) 28 is held.

[0018] The lead wire 32 which the upper part edge of an internal electrode 24 is held at the up packing 30 inserted in the interior of an outer case 22 by suiting, and was connected to the internal electrode 24 penetrates this up packing 30, and is taken out outside. As for an internal electrode 24, at this time, it is desirable not to penetrate the up packing 30, but to insert even in abbreviation one half extent of the thickness of the up packing 30, and to make it only lead wire 32 penetrate the up packing 30. This is for preventing that an internal electrode 24 is put back up, when it is filled up with the compressed air in an outer case 22 and the upper part air chamber 34 of internal liquid 28 is pressurized so that it may be for protecting and may mention later that an internal electrode 24 runs through the up packing 30, and projects upwards when stuffing the up packing 30 into the interior of an outer case 22. Upper part open end 22b of an outer case 22 is closed by cap 36.

[0019] In this example, a stoma 38 is drilled in the side face of an outer case 22, and the side -face packing 40 is attached in this hole 38. It is made for the attaching position of the side -face packing 40 to be located in the upper part air chamber 34 of the internal liquid 28 held in the outer case 22. Moreover, although side-face packing 40 can be made into the configuration of arbitration, in this example, it considers as the shape of a cylindrical shape in which the circular sulcus 42 for attaching in the stoma 38 of an outer case 22 was formed, and is produced with a spring material. Therefore, the outer diameter of a circular sulcus 42 is made larger than the bore of the outer case stoma 38, therefore the side -face packing 40 fits into this stoma 38 in a from cartridge, and is fixed to it.

[0020] In the reference electrode 20 of this invention of the above -mentioned configuration, the upper part air chamber 34 of an outer case 22 is pressurized using a compressed -air supply means 50 like a syringe (syringe). That is, according to this example, the compressed -air supply means 50 has a cylinder 52 and the piston 54 which fitted into this cylinder 52 free [ sliding ], and the needlelike pipe 56 which cut a tip like a hypodermic needle aslant is attached at the tip of a cylinder 52. Therefore, this needlelike pipe 56 can reach to the upper part air chamber 34 of an outer case 22 by thrusting that tip section 56a into the side-face packing 40 which is an elastic body, as shown in drawing 1. By operating a piston 54 in the direction of an arrow head after that, the compressed air is injected into the upper part air chamber 34 through this needlelike pipe 56, and this air chamber 34 is pressurized.

[0021] After an air chamber 34 serves as a predetermined pressure, the needlelike pipe 56 is sampled from the side-face packing 40. Since the side-face packing 40 is an elastic body at this time, the hole after extracting the needlelike pipe 56 will be closed with that elasticity. That is, the side -face packing

40 plays the role of a check valve.

[0022] Although the side-face packing 40 which makes the function like \*\*\*\* can be produced using the thing of arbitration if it is an electrical insulation material which has rubber elasticity by 2-30mm in thickness, it has nitrile rubber (NBR), chloroprene rubber (CR), ethylene propylene rubber (EPM), silicone rubber (Si), a fluororubber (FPM), etc., for example. In addition, since it has exposed into atmospheric air, as for the external surface of the side-face packing 40, it is desirable at this example to produce by the small elastomer of gas permeability (polymeric materials which have rubber-like elasticity), for example, isobutylene isoprene rubber.

[0023] moreover, although various dimension configurations of the side-face packing 40 could be boiled and designed, the good result was able to be obtained by considering as the outer diameter of 5-10mm, and die length of 3-10mm.

[0024] On the other hand, when the high ingredient of gas permeability is used like silicone rubber as an ingredient of said up packing 30, as shown in drawing 1, it is desirable to be filled up with adhesives 58 on the up packing 30, and it is desirable as adhesives for restoration also in this case, few ingredients, for example, the epoxy resin adhesive, of gas permeability. According to this invention persons' experimental result, silicone system adhesives had large gas permeability, for example, it turned out that the air of 3 kg/cm<sup>2</sup> (gage pressure) will fall even to 1 kg/cm<sup>2</sup> (gage pressure) in three days. On the other hand, even if epoxy resin adhesive passed on the 3rd, there was no fall of a pressure substantially. Furthermore, building envelope 36A formed with cap 36 if needed can also be filled up with the same thing as the above-mentioned adhesives for restoration.

[0025] Although a water solution or gel liquid is sufficient as the internal liquid 28 held in an outer case 22 with the reference electrode 20 of this invention, the gel liquid of the pressure percentage reduction of the outer case air chamber 34 is smaller. As gel liquid, there is a potassium chloride solution gelled, for example by hydroxyethyl cellulose, the carboxymethyl cellulose, or the acrylamide polymer.

[0026] Moreover, liquid junction 26 has the high resistance to a pressure, and if it is the good ingredient of absorptivity, it is producible using the thing of arbitration. For example, the porosity polyethylene which has absorptivity, porosity polyester, a porosity acrylic, etc. can be used. Especially the porous ceramics with which water absorption is made into 5-15% are especially effective from being repeatedly exposed to a 120-130-degree C elevated-temperature steam for sterilization, when using the reference electrode 20 of this invention in fermentation industry etc. in addition, the volume (V0) of \*\*\*\* [as opposed to / with water absorption / the volume (V) of the whole liquid junction 26 with this application specification] -- comparatively (V0 / V) -- meaning.

[0027] In this example, the ceramics of 10% of water absorption was able to be used for liquid junction 26, the potassium chloride solution gelled as internal liquid 28 at hydroxyethyl cellulose was able to be used, and the result with the good time of producing the side-face packing 40 by penetrable small isobutylene isoprene rubber was still more specifically able to be obtained. Moreover, when the internal pressure after fixed time amount progress declined, again, the needlelike pipe 56 was able to be thrust into the side-face packing 40, and it was able to pressurize.

[0028] As mentioned above, since extract the needlelike pipe 56 to the packing 40 which was fixed according to this example, stab it with it, it thrusts free, the compressed air is poured in and the needlelike pipe 56 is considered as the configuration extracted after that, pressures are 2.5 kg/cm<sup>2</sup>. If it is less than, the disposable syringe of a low price can be used without using a large-sized compressed-air feeder like a compressor. Especially in this example which attached packing 40 in the lateral portion of the reference electrode outer case 22, while using this reference electrode 20 for measurement, also when there is pressure reduction, it can pressurize repeatedly.

[0029] One example when the pressure type reference electrode 20 concerning this invention is used for example 2 drawing 2 by the composite electrode 1 is shown.

[0030] The pressure type composite electrode 1 is used as a glass electrode in this example, and it has the container liner 4 which constitutes the measuring electrode 2 equipped with induction film 2a, and the outer case 22 which constitutes the reference electrode 20 arranged in the said alignment to this container liner 4.

[0031] The buffer solution 8 is held in the internal room 6 formed with a container liner 4 in order to form a measuring electrode 2, and an electrode 10 is arranged in it. The lead wire 14 which penetrates the plug 12 which closes the upper part of the internal room 6, and extends is connected to this electrode 10. Moreover, internal liquid (reference electrolytic solution) 28 is held in the annular room 34 formed with a container liner 4 and an outer case 22 in order to form a reference electrode 20, and an internal electrode 24 is arranged. Liquid junction 26 is formed in the lower part edge of the annular room 34.

[0032] The internal electrode 24 is attached in the annular up packing 30 inserted in the annular room 34 by suiting in this example. Moreover, the lead wire 32 connected to the internal electrode 24 penetrates this up packing 30, and is taken out outside. At this time, it is desirable for an internal electrode 24 not to penetrate the up packing 30, but to insert it to the abbreviation one half of the thickness of the up packing 30 for the reason explained in the example 1, and to make it only lead wire 32 penetrate the up packing 30.

[0033] Also in this example, as it is similarly located in the side face of an outer case 22 with the example 1 having explained at the especially annular air chamber 34, the side-face packing 40 is formed. An ingredient, a dimension configuration, the compressed-air supply means 50, etc. of the side-face packing 40 are made the same as an example 1, and the explanation beyond this is omitted.

[0034] Also in this example, the same operation effectiveness as an example 1 can be acquired.

[0035] Other examples of the pressure type reference electrode 20 built over this invention at example 3 drawing 3 are shown.

[0036] Although the pressure type reference electrode 20 of this example is considered as the same configuration as the reference electrode 1 of the example 1 shown in drawing 1, every time the side-face packing 40 of an example 1 is formed, it does not break it, but merely differ in that installation of the compressed air into the air chamber 34 of a reference electrode 20 is performed through the up packing 30. Therefore, in this example, the up packing 30 is produced with the above-mentioned spring material like the same elastomer as the side-face packing 40 of an example 1 which has rubber elasticity.

[0037] Moreover, in this example, since the needlelike pipe 56 of the compressed-air supply means 50 is considered as the configuration thrust into the up packing 30, before installing cap 36 in the reference electrode upper part, pressurization in the annular room 34 is performed.

[0038] Furthermore, when having already filled up with the adhesives 58 for up packing immobilization, in order for the needlelike pipe 56 to also make these adhesives 58 penetrate, even if adhesives 58 are after hardening, it is required that it should have rubber elasticity. Therefore, as adhesives 58, silicone resin is suitable.

[0039] Also in this example, the same operation effectiveness as an example 1 can be acquired.

[0040] Other examples when the pressure type reference electrode 20 concerning this invention is used for example 4 drawing 4 by the composite electrode are shown.

[0041] The pressure type composite electrode 1 of this example is considered as the same configuration as the composite electrode 1 of the example 2 shown in drawing 2, and every time the side-face packing 40 of an example 2 is formed, it does not break it, but they merely differ in that installation of the compressed air into the annular room 34 of a reference electrode 20 is performed through the up packing 30. Therefore, the up packing 30 is produced with the above-mentioned spring material like an elastomer like [this example] the case of an example 3.

[0042] Moreover, in this example, since the needlelike pipe 56 of the compressed-air supply means 50 is considered as the configuration thrust into the up packing 30 like the case of an example 3, before installing cap 36 in the composite electrode upper part, pressurization in the annular room 34 is performed.

[0043] Furthermore, also in this example, when having already filled up with the adhesives 58 for up packing immobilization, in order for the needlelike pipe 56 to also make these adhesives 58 penetrate, even if adhesives 58 are after hardening, it is required that it should have rubber elasticity. Therefore, as adhesives 58, silicone resin is suitable.

[0044] Also in this example, the same operation effectiveness as an example 2 can be acquired.

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

**[Drawing 1]** It is the sectional view of one example of the pressure type reference electrode concerning this invention.

**[Drawing 2]** It is the sectional view of other examples of the pressure type reference electrode concerning this invention.

**[Drawing 3]** It is the sectional view of the example of further others of the pressure type reference electrode concerning this invention.

**[Drawing 4]** It is the sectional view of the example of further others of the pressure type reference electrode concerning this invention.

**[Drawing 5]** It is the sectional view of the conventional pressure type reference electrode.

**[Drawing 6]** It is the sectional view of the conventional pressure type reference electrode.

**[Drawing 7]** It is the sectional view of the conventional pressure type reference electrode.

**[Description of Notations]**

1 Composite Electrode

2 Measuring Electrode

4 Container Liner

20 Reference Electrode

22 Outer Case

24 Internal Electrode

26 Liquid Junction

28 Internal Liquid

30 Up Packing

34 Air Chamber (Annular Room)

40 Side-Face Packing

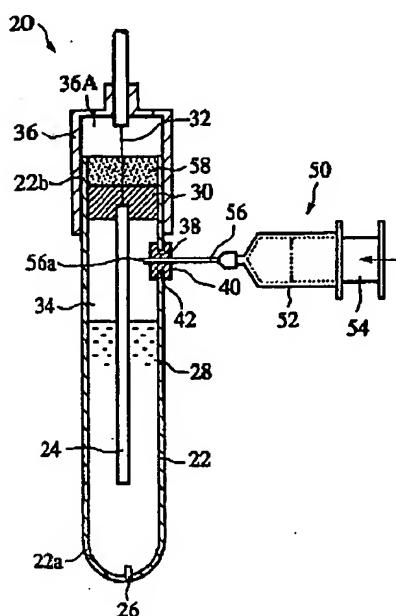
50 Compressed-Air Supply Means

56 Needlelike Pipe

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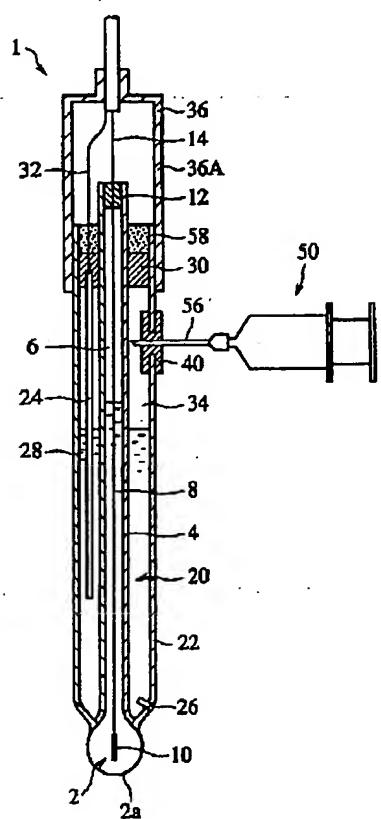
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Drawing selection drawing 1



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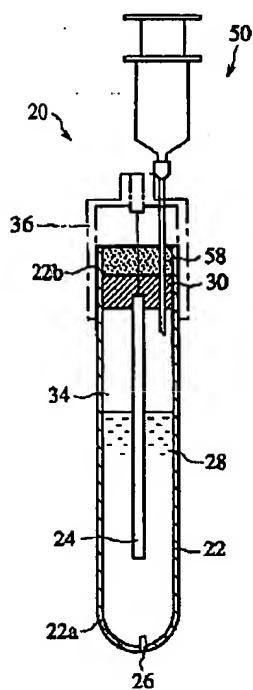
Drawing selection drawing 2



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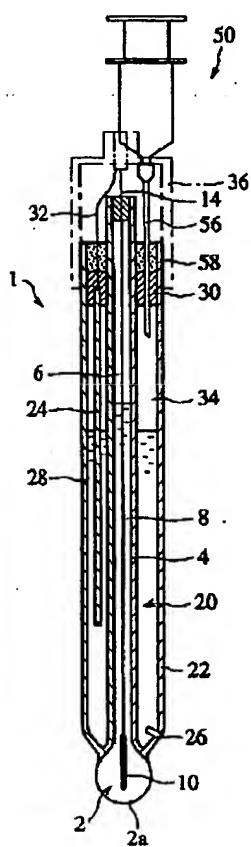
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Drawing selection drawing 3

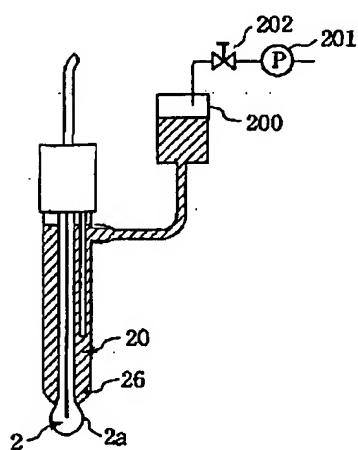


[Translation done.]

Drawing selection drawing 4



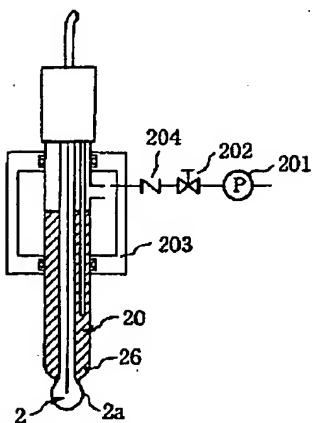
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Drawing selection [drawing 5 

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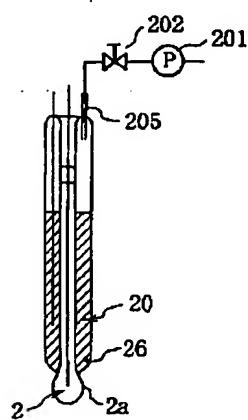
Drawing selection drawing 6



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Drawing selection drawing 7



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